

CLAIMS

1. A system comprising:

a polymeric article including a three-dimensionally periodic structure of a plurality of periodically occurring separate domains, with at least a first and a second domain each being topologically continuous, and with said first domain comprising a polymeric species containing an inorganic species capable of forming a ceramic oxide, said inorganic species present in an amount of at least about 3 atomic% based on the total number of atoms in the first domain.

2. A system comprising:

a polymeric article including a periodic structure of a plurality of periodically occurring separate domains, with at least a first and a second domain, said first domain comprising a polymeric species containing an inorganic species capable of forming a ceramic oxide, said polymeric species containing an inorganic species capable of forming a ceramic oxide being formed of a polymerized monomer containing an inorganic species capable of forming a ceramic oxide, said inorganic species present in an amount of at least about 3 atomic% based on the total number of atoms in the first domain, and said second domain comprising a polymeric species not containing a sufficient quantity of inorganic species to be capable of forming a ceramic oxide, where the polymerized monomer containing an inorganic species capable of forming a ceramic oxide has a glass transition temperature of at least about 0 degrees C, and polymers comprising the polymeric article have an average molecular weight of at least about 30,000 Da.

3. A system comprising:

an article including a periodic structure of a plurality of periodically occurring separate domains having a plurality of boundaries between said domains defining a plurality of interfaces, with at least a first and second domain having a boundary therebetween defining at least one interface, and said first domain including an oxidized polymeric species forming an inorganic oxide ceramic and said second domain at least partially comprised of void space, where an interface between the domains is at least partially comprised of the inorganic oxide ceramic, said inorganic oxide ceramic forming a layer at at least a portion of said interface that

is at least 1 nm thick.

4. A system comprising:

a block copolymeric species having at least two blocks A and B, the blocks A and B being incompatible with each other such that the block copolymeric species is self-assembleable into a three-dimensionally periodic polymeric article including a structure of a plurality of separate domains, with at least a first and a second domain each being topologically continuous and defined by association of similar blocks of the copolymeric species, with at least block A comprising a polymeric species containing an inorganic species capable of forming a ceramic oxide, said inorganic species present in an amount of at least about 3 atomic% based on the total number of atoms in block A.

5. A method comprising:

processing a block copolymeric species, including at least one block comprising a polymeric species containing an inorganic species capable of forming a ceramic oxide, said inorganic species present in an amount of at least about 3 atomic% based on the total number of atoms in said block, to produce a phase separated multi-domain three-dimensionally periodic polymeric article including a structure of a plurality of separate domains, with at least a first and a second domain each being topologically continuous and defined by association of similar blocks of the copolymeric species.

6. A system comprising:

a block copolymeric species having at least two blocks A and B, the blocks A and B being incompatible with each other such that the block copolymeric species is self-assembleable into a periodic polymeric article including a structure of a plurality of separate domains, with at least a first and a second domain each being defined by association of similar blocks of the copolymeric species, with at least one of said blocks comprising a polymeric species containing an inorganic species capable of forming a ceramic oxide, said polymeric species containing an inorganic species capable of forming a ceramic oxide being formed of a polymerized monomer containing an inorganic species capable of forming a ceramic oxide, and at least one other block comprising a polymeric species not containing a sufficient quantity of inorganic species to be capable of forming a ceramic oxide; said

polymerized monomer having a content of said inorganic species of at least about 3 atomic% based on the total number of atoms in said polymerized monomer, and a glass transition temperature of at least about 0 degrees C, said block copolymeric species having an average molecular weight of at least about 30,000 Da.

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7. A method comprising:

processing a block copolymeric species, including at least one block comprising a polymeric species containing an inorganic species capable of forming a ceramic oxide, said polymeric species containing an inorganic species capable of forming a ceramic oxide being  
10 formed of a polymerized monomer containing an inorganic species capable of forming a ceramic oxide, and at least one other block comprising a polymeric species not containing a sufficient quantity of inorganic species to be capable of forming a ceramic oxide, with said polymerized monomer having a content of said inorganic species of at least about 3 atomic% based on the total number of atoms in said polymerized monomer and a glass transition  
15 temperature of at least about 0 degrees C, and with said block copolymeric species having an average molecular weight of at least about 30,000 Da, to produce a phase separated multi-domain periodic polymeric article including a structure of a plurality of separate domains, with at least a first and a second domain each being defined by association of similar blocks of the copolymeric species.

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8. The system or method of any of claims 1, 4, or 5 wherein said polymeric species containing an inorganic species capable of forming a ceramic oxide comprises a silicon-containing polymeric species.

25 9. The system or method of any of claims 2, 6, or 7 wherein said polymerized monomer containing an inorganic species capable of forming a ceramic oxide comprises a silicon-containing polymeric species.

30 10. The system or method of any of claims 1, 2, 4-7 wherein the polymeric article includes a polymeric material self-assembled into a periodic structure of a plurality of periodically occurring separate domains, comprising at least the first and the second domain.

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11. The system or method of any of claims 1, 4, or 5 wherein said second domain comprises a polymeric species not containing a sufficient quantity of inorganic species to be capable of forming a ceramic oxide.

5 12. The system of claim 3, wherein said void space is formed by at least partial removal of a precursor polymeric species not containing a sufficient quantity of inorganic species to be capable of forming a ceramic oxide from a precursor periodic polymeric article.

10 13. The system of claim 12, wherein the precursor periodic polymeric article includes a polymeric material self-assembled into a periodic structure of a plurality of periodically occurring separate domains, with at least a first and a second domain.

15 14. The system or method of any of claims 2, 6, 7, or 11, wherein said second domain at least partially comprises void space formed by at least partial removal of the polymeric species not containing a sufficient quantity of inorganic species to be capable of forming a ceramic oxide from the periodic structure.

20 15. The system or method of claim 14, wherein said first domain includes an inorganic oxide ceramic formed by oxidation of the polymeric species containing an inorganic species.

25 16. The system or method of any of claims 1, 4, or 5 wherein said polymeric species containing an inorganic species capable of forming a ceramic oxide is comprised of a polymerized monomer, the monomer containing an inorganic species capable of forming a ceramic oxide.

17. The system or method of any of claims 1, 2, 4-7, or 12 wherein the first and second domains of the polymeric article comprise a block copolymeric species having at least two blocks A and B that are assembled into the first and second domains respectively.

30 18. The system or method of claim 17, wherein the block copolymeric species has at least three blocks A, B, and C.

28. The system or method of claims 3 or 14, wherein the article has at least a first side and a second side with at least one void space providing a continuous pathway for fluid communication between said first side and said second side so that the article functions as a membrane.

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29. The method of claims 5 or 7, comprising allowing the ~~block copolymeric species~~ to self-assemble into the phase separated polymeric multi-domain periodic structure.

30. An article comprising:

5 a periodic structure of a plurality of periodically occurring separate domains, with at least a first and a second domain, said first and second domains having a structure defined by self assembly of at least one polymeric species and with at least one domain comprising a molded structure formed of at least one of a liquid or solid material that cannot be formed into a periodic structure by self-assembly, with each domain that is not formed of said material  
10 being essentially free of said material.

31. The system, method, or article of any of claims 2, 3, 6, 7, or 30, wherein the article has an at least three-dimensionally periodic structure.

15 32. The system, method, or article of claims 26 or 30, wherein said material is a polymer that cannot be formed into a periodic structure by self-assembly.

33. The system, method, or article of claim 32, wherein said polymer that cannot be formed into a periodic structure by self-assembly is a fluorine-containing polymer.

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34. The system, method, or article of claim 33, wherein said polymer that cannot be formed into a periodic structure by self-assembly is poly(tetrafluoroethylene).

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25 35. The system, method, or article of claims 26 or 30 wherein said material is a conducting polymer.

36. The system, method, or article of claims 26 or 30, wherein said material is a metal.

30 37. The system, method, or article of claim 36, wherein said metal is a liquid having a melting temperature of at least about 400 degrees C.

38. The system, method, or article of claims 26 or 30, wherein said material is a material

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having a dielectric constant greater than three.

39. The system, method, or article of claims 26 or 30, wherein said material is a magnetic material.

40. The system, method, or article of claim 39, wherein said magnetic material is disposed on the surface of a substrate.

41. The system, method, or article of any preceding claim, wherein the structure has a photonic band gap in at least one direction for electromagnetic radiation of at least one wavelength within the range of about 20 nm to about 1  $\mu\text{m}$ .

42. The system, method, or article of any preceding claim, wherein the article has an at least one-dimensionally periodic structure.

43. The system, method, or article of any preceding claim, wherein the article has an at least two-dimensionally periodic structure.

44. The article of claim 30, wherein the domains that are essentially free of said material comprise void space.

45. The article of claim 30, wherein the domains that are essentially free of said material are at least partially comprised of an inorganic oxide ceramic.

46. A membrane comprising:  
a periodic structure, including a plurality of periodically occurring void spaces defining a plurality of pores, the membrane having at least a first side and a second side, where at least one of said pores provides a continuous pathway for fluid communication between said first side and said second side, said at least one pore having a surface at least partially comprised of an oxidized polymeric species forming an inorganic oxide ceramic.

47. A mold comprising:

a periodic structure, including a plurality of periodically occurring void spaces therein, where at least one of said void spaces provides a continuous pathway for fluid communication with the atmosphere surrounding said structure, with at least one void space providing a continuous pathway for fluid communication with the atmosphere surrounding said structure having a surface at least partially comprised of an oxidized polymeric species forming an inorganic oxide ceramic, said inorganic oxide ceramic forming a layer at least 1 nm thick at at least a portion of said surface.

48. A method comprising:

creating a periodic structure of a material by providing a mold comprising a periodic structure including a plurality of periodically occurring void spaces, with at least one void space having a surface at least partially comprised of an oxidized polymeric species forming an inorganic oxide ceramic, said inorganic oxide ceramic forming a layer at least 1 nm thick; and

at least partially filling said void space with said material.

~~49. The membrane, mold, or method of any of claims 46-48, wherein said void spaces have a characteristic minimum dimension of between 1 nm and 1  $\mu$ m.~~

50. The membrane of claim 46, wherein said pores are present at the surface of said first side and said second side at a density of at least about  $10^3$  per square centimeter.

51. The membrane of claim 46, said pores are present at the surface of said first side and said second side at a density of at least about  $10^{10}$  per square centimeter.

~~52. The membrane, mold, or method of any of claims 46-48, wherein said inorganic oxide ceramic is comprised of an oxidized silicon-containing polymeric species.~~

53. The membrane of claim 46, wherein the membrane forms a coating layer on a substrate.

54. The membrane of claim 53, wherein the coating layer is thermally stable at



temperatures of at least about 400°C.

55. The membrane, mold, or method of any of claims 46-48, wherein the structure is one-dimensionally periodic.

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56. The membrane, mold, or method of any of claims 46-48, wherein the structure is two-dimensionally periodic.

57. The membrane, mold, or method of claim 56, wherein said void spaces are in the shape of essentially circular cylinders.

58. The membrane, mold, or method of claim 57, wherein said void spaces are non-overlapping and non-intersecting.

59. The membrane, mold, or method of any of claims 46-48, wherein the structure is three-dimensionally periodic.

60. The membrane, mold, or method of claim 59, wherein said void spaces form an interconnected continuous network of pathways within said structure having a plurality of nodes.

61. The membrane, mold, or method of claim 60, wherein said void spaces are made conducting, thus forming a conducting network.

62. A photonic band gap article comprising:

a periodic structure of a plurality of periodically occurring separate domains, with at least a first and a second domain, said structure including at least one interface defined by a surface of contact between said first domain and said second domain, which interface is at least partially comprised of a layer of an oxidized polymeric species forming an inorganic oxide ceramic, said layer being at least about 1 nm thick, where the structure inhibits the propagation of electromagnetic radiation of at least one wavelength within the range of about 20 nm to about 1  $\mu$ m.

63. A low dielectric constant material comprising:

a periodic structure of a plurality of periodically occurring separate domains, with at least a first and a second domain, at least one domain being at least partially comprised of void space, and at least one other domain being at least partially comprised of an inorganic oxide ceramic; said structure having a dielectric constant less than about 3.

64. A high dielectric constant material comprising:

a periodic molded structure of a plurality of periodically occurring separate domains, with at least a first and a second domain, said structure having a dielectric constant greater than about 3.

65. The high dielectric constant material of claim 64, where said structure has a dielectric constant greater than about 5.

66. The high dielectric constant material of claim 64, where said structure has a dielectric constant greater than about 8.

67. The high dielectric constant material of claim 64, where said structure has a dielectric constant greater than about 8.5.

68. The high dielectric constant material of claim 64, where said structure has a dielectric constant greater than about 10.

69. A method comprising:

forming a polymeric article including a periodic structure of a plurality of periodically occurring separate domains, with at least a first and a second domain, said first domain comprising a polymeric species containing an inorganic species capable of forming capable of forming a ceramic oxide, said inorganic species present in an amount of at least about 3 atomic% based on the total number of atoms in said first domain;

at least partially removing at least one domain from the structure; and  
at least partially oxidizing the structure to form an inorganic oxide ceramic.

70. The method of claim 69, wherein said article is formed to include at least one domain comprising a polymeric species not containing a sufficient quantity of inorganic species to be capable of forming an inorganic oxide ceramic.

5 71. The method of claim 70, wherein said at least one domain comprising a polymeric species not containing a sufficient quantity of inorganic species to be capable of forming an inorganic oxide ceramic is formed of a polymeric species that has a chain with a plurality of unsaturated bonds.

10 72. The method of claim 70, comprising allowing the polymeric article to form by self-assembly of polymeric material into a periodic structure of a plurality of periodically occurring separate domains, with at least a first and a second domain.

15 73. The method of claim 72, wherein the polymeric article is formed by self-assembly of a block copolymeric species having at least two blocks A and B that are assembled into the first and second domains respectively.

20 74. The method of claim 69, wherein the polymeric species containing an inorganic species capable of forming an inorganic oxide ceramic comprises a silicon-containing polymeric species.

25 75. The method of claim 70, wherein said article is formed with said at least one domain comprising a polymeric species not containing a sufficient quantity of inorganic species to be capable of forming an inorganic oxide ceramic comprising a non-silicon-containing polymeric species.

30 76. The method of claim 70, wherein said at least one domain comprising a polymeric species not containing a sufficient quantity of inorganic species to be capable of forming an inorganic oxide ceramic is at least partially removed in the removing step.

77. The method of claim 69, wherein said at least one domain comprising a polymeric species containing an inorganic species capable of forming an inorganic oxide ceramic is

oxidized in the oxidizing step.

78. The method of claim 69, wherein the removing step and the oxidizing step are performed simultaneously.

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79. The method of claim 69, wherein the removing step is performed prior to the oxidizing step.

80. The method of claim 69, wherein the oxidizing step is performed prior to the removing step.

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81. ~~The method of any of claims 69, 78-80, wherein the removing step includes exposing the article to a chemical oxidizer.~~

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82. The method of claim 81, wherein the chemical oxidizer is ozone.

83. The method of claim 82, wherein the ozone is provided as a gas.

84. The method of claim 82, wherein the ozone is provided in a liquid solution.

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85. ~~The method of any of claims 69, 78-80, wherein the removing step includes exposing the article to radiation.~~

86. The method of claim 85, wherein the radiation is ultraviolet light.

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87. ~~The method of any of claims 69, 78-80, wherein the removing step includes exposing the article to oxygen plasma etching.~~

88. The method of claim 87, wherein the article is exposed to oxygen reactive ion etching.

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89. ~~The method of any of claims 69, 78-80, wherein the removing step includes exposing the article to a combination of a chemical oxidizer and radiation.~~

90. The method of any of claims 69, 78-80, wherein the removing step includes exposing the article to a combination of a chemical oxidizer and oxygen plasma etching.

91. The method of any of claims 69, 78-80, wherein the removing step includes exposing the article to a combination of a radiation and oxygen plasma etching.

92. The method of any of claims 69, 78-80, wherein the removing step includes exposing the article to an electron beam.

93. The method of any of claims 69, 78-80, wherein the removing step includes exposing the article to heat.

94. The method of any of claims 69, 78-80, wherein the removing step includes exposing the article to a base.

95. The method of any of claims 69, 78-80, wherein the removing step includes exposing the article to a solvent.

96. The method of any of claims 69, 78-80, wherein the oxidizing step includes exposing the article to a chemical oxidizer.

97. The method of claim 96, wherein the chemical oxidizer is ozone.

98. The method of claim 97, wherein the ozone is provided as a gas.

99. The method of claim 97, wherein the ozone is provided in a liquid solution.

100 The method of any of claims 69, 78-80, wherein the oxidizing step includes exposing the article to radiation.

101. The method of claim 100, wherein the radiation is ultraviolet light.

Sub B12 102. The method of any of claims 69, 78-80, wherein the oxidizing step includes exposing the article to oxygen plasma etching.

103. The method of claim 102, wherein the article is exposed to oxygen reactive ion etching.

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104. The method of any of claims 69, 78-80, wherein the oxidizing step includes exposing the article to a combination of a chemical oxidizer and radiation.

Sub B13 105. The method of any of claims 69, 78-80, wherein the oxidizing step includes exposing the article to a combination of a chemical oxidizer and oxygen plasma etching.

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106. The method of any of claims 69, 78-80, wherein the oxidizing step includes exposing the article to a combination of a radiation and oxygen plasma etching.

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15 107. A method for forming a conducting network comprising:  
providing a polymeric article including a periodic structure of a plurality of  
periodically occurring separate domains, with at least a first and a second domain;  
at least partially removing at least one domain to form at least one void space; and  
at least partially filling said void space with a conducting material to form at least one  
20 conducting pathway.

108. The method of claim 107 further comprising before the filling step, the step of at least partially oxidizing the structure to form an inorganic oxide.

25 109. A method comprising:  
at least partially oxidizing a polymeric article, the article including a periodic structure  
of a plurality of periodically occurring separate domains, with at least a first and a second  
domain, said first domain comprising a polymeric species containing an inorganic species  
capable of forming a ceramic oxide, said inorganic species present in an amount of at least  
30 about 3 atomic% based on the total number of atoms in said first domain, where at least one  
domain of said structure has been at least partially removed, to form an inorganic oxide  
ceramic.

110. A method for forming a magnetic article comprising:  
forming a polymeric article including a periodic structure of a plurality of periodically  
occurring separate domains, with at least a first and a second domain;  
at least partially removing at least one domain to form at least one void space; and  
5 adding a magnetic material to the void space so as to at least partially fill the void  
space with the magnetic material.

111. A method for forming a magnetic article comprising:  
forming on a substrate a polymeric article including a periodic structure of a plurality  
10 of periodically occurring separate domains, with at least a first and a second domain;  
at least partially removing at least one domain to form at least one void space; and  
adding a magnetic material to at least one void space.

112. The method of claim 110, wherein the article is formed on a substrate during the  
15 forming step.

113. The method of claims 110 or 111, further comprising before the adding step:  
at least partially oxidizing the structure to form an inorganic oxide.

Sub Pkt 114. The method of claims 111 or 112, further comprising:  
removing the article from the substrate, while leaving behind on the substrate at least a  
portion of the magnetic material.

25 115. The method of claims 111 or 112, wherein the forming step comprises:  
providing the substrate;  
coating the substrate with a polymeric layer; and  
converting the layer into said polymeric article.

30 116. The method of claim 111 or 112, wherein the forming step comprises:  
providing the substrate; and  
attaching said polymeric article to the substrate.

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Cont 117. The method of claims 110 or 111, wherein at least one domain of the polymeric article is at least partially oxidized during the removing step.

118. The method of claim 111, wherein the adding step comprises at least partially filling  
5 said void space with the magnetic material.

119. The method of claims 110 or 111, wherein the polymeric article has an at least one-  
dimensionally periodic structure.

10 120. The method of claims 111 or 112, wherein the polymeric article has an at least two-  
dimensionally periodic structure.

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121. The method of claims 110 or 111, wherein the polymeric article has a three-  
dimensionally periodic structure.

15 122. The method of claims 110 or 111, wherein domains that are at least partially removed  
during the removing step are non-interconnected.

123. The method of claims 111 or 112, wherein during the adding step, the magnetic  
20 material is deposited into the void space by electrodeposition.

124. The method of claim 123, wherein at least a portion of the a surface of the substrate in  
contact with the polymeric article comprises an electrical conductor.

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125. The method of claims 110 or 111, wherein during the adding step, the magnetic  
material is deposited into the void space by vapor deposition.

126. The method of claim 125, wherein the magnetic material is deposited by chemical  
vapor deposition.

30 127. The method of claim 125, wherein the magnetic material is deposited by physical vapor  
deposition.



128. The method of claim 127, wherein the magnetic material is deposited by evaporation.

129. The method of claim 127, wherein the magnetic material is deposited by sputtering.

5 130. The method of claim 120, wherein the at least one domain at least partially removed during the removing step is oriented with a longitudinal axis that is non-coplanar to a surface of the substrate in contact with the polymeric article.

10 131. The method of claim 120, wherein the at least one domain at least partially removed during the removing step is oriented with a longitudinal axis that is essentially perpendicular to a surface of the substrate in contact with the polymeric article.

132. The method of claim 120, wherein the at least one domain at least partially removed during the removing step is essentially cylindrical in shape.

15 133. A magnetic article comprising:

a three-dimensionally periodic structure of a plurality of periodically occurring separate domains, with at least a first and a second domain, at least one domain having a characteristic dimension not greater than 1  $\mu\text{m}$  and including a magnetic material, with each domain that  
20 includes a magnetic material being non-interconnected.

134. A magnetic article comprising:

a periodic structure of a plurality of periodically occurring separate domains, with at least a first and a second domain, said first and second domains having a structure defined by  
25 self-assembly of at least one polymeric species, at least one domain including a magnetic material, with each domain that includes a magnetic material being non-interconnected.

135. The article of claims 133 or 134, wherein the at least one domain including a magnetic material is at least partially surrounded by void space.

136. The article of claims 133 or 134, wherein the at least one domain including a magnetic material is at least partially surrounded by a polymeric material.

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137. The article of claims 133 or 134, wherein the at least one domain including a magnetic material is at least partially surrounded by an inorganic oxide ceramic.

138. The article of claims 133 or 134, further comprising a substrate in contact with a surface of the at least one domain including a magnetic material.

139. The article of claim 138, wherein a surface of the substrate in contact with the surface of at least one domain including a magnetic material comprises an electrical conductor.

140. The article of claims 133 or 134, wherein the at least one domain including a magnetic material has a characteristic dimension between about 10 nm and about 50 nm.

141. The article of claims 133 or 134, wherein domains including a magnetic material are separated from each other by a minimum distance of between about 1 nm and about 20 nm.

142. The article of claims 133 or 134, wherein the at least one domain including a magnetic material consists essentially of the magnetic material.

143. The article of claims 133 or 134, wherein the magnetic material is selected from at least one of cobalt, nickel, iron, alloys of cobalt and platinum, alloys of cobalt and iron, oxides thereof, and barium ferrite.

144. The article of claim 134, wherein the periodic structure is at least one-dimensionally periodic.

145. The article of claim 134, wherein the periodic structure is at least two-dimensionally periodic.

146. The article of claim 145, wherein the at least one domain including a magnetic material is oriented with a longitudinal axis that is non-coplanar to a surface of a substrate in contact with a surface of the domain including a magnetic material.

147. The article of claim 145, wherein the at least one domain including a magnetic material is oriented with a longitudinal axis that is essentially perpendicular to a surface of a substrate in contact with a surface of the domain including a magnetic material.

- 5 148. The article of claim 145, wherein the at least one domain including a magnetic material is essentially cylindrical in shape.

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